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Adducts of Bis(*O,O*-alkylene dithiophosphates) of Nickel(II) with 2,9-Dimethyl-1,10-phenanthroline. X-ray Crystal and Molecular Structure of (2,9-Dimethyl-1,10-phenanthroline)bis(4,4,5,5-tetramethyl-1,3,2-dioxaphospholane-2-thione-2-thiolato)nickel(II)

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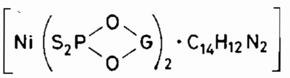
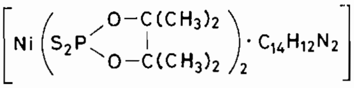
Abstract

Paramagnetic, pentacoordinated 2,9-dimethyl-1,10-phenanthroline adducts of bis(*O,O*-alkylene dithiophosphates) of nickel(II) with the general formula



(where $G(OH)_2$ = 2,3-dimethylbutane-2,3-diol, 2-methylpentane-2,4-diol and butane-2,3-diol) have been prepared by the reactions of *O,O*-alkylene dithiophosphates of nickel(II) with 2,9-dimethyl-1,10-phenanthroline in a 1:1 molar ratio. IR, electronic spectral and magnetic measurements have been used to investigate plausible structure of these complexes. The crystal structure of



shows both chelating and monodentate dithiophosphate moieties. Crystals of the above adducts are monoclinic, space group $P2_1/c$, a = 20.077(1), b = 11.599(2), c = 14.929(2) Å, β = 107.65(5)° and $Z = 4$.

The structure of the compound was refined to R = 0.070 for 2809 unique observed diffractometer data. The structure may be interpreted as involving a pentacoordinated nickel atom with a distorted trigonal bipyramidal geometry. The equatorial positions are occupied by N atoms of 2,9-dimethyl-1,10-phenanthroline (Ni–N(av.) = 2.01 Å), one axial (Ni–S(3) = 2.499(3) Å) and one equatorial (Ni–S(4) = 2.344(3) Å) position by the S atoms of a bidentate *O,O*-alkylene dithiophosphate moiety, and the remaining axial position (Ni–S(1) = 2.398(3) Å) is occupied by the S atom of the other monodentate alkylene dithiophosphate moiety.

Introduction

Square planar nickel(II) *O,O*-dialkyl dithiophosphates $[Ni(S_2P(OR)_2)_2]$, and their octahedral 1:2 adducts $[Ni(S_2P(OR)_2)_2 \cdot 2L]$ with monodentate nitrogen donor ligands have been intensively investigated for about three decades [1–4]. In these complexes, the dithiophosphate moieties invariably behave as chelating bidentate. The formation of five coordinated intermediate monoadduct species is indicated by spectrophotometric titration between $[Ni(S_2P(OC_2H_5)_2]_2$ and pyridine or picolines [5]. With phosphorus donor ligands, however, a few such five coordinated complexes, e.g. $[Ni(S_2P(OC_2H_5)_2)_2 \cdot PR_3]$ (R = Bu, Ph) have actually been isolated in the solid state [6, 7].

The above studies have been extended to the adducts of $[Ni(S_2P(OR)_2)_2]$ with bidentate nitrogen donor ligands (e.g. phenanthroline [8] and bipyridyl [9]). In these cases, octahedral 1:1 complexes are usually formed. A similar 1:1 complex of $[Ni(S_2P(OCH_3)_2)_2]$ with the sterically crowded ligand, 2,9-dimethyl-1,10-phenanthroline [10], however, shows an unusual structure which incorporates five coordinated nickel surrounded by two nitrogen and three sulphur atoms. Thus one of the dithiophosphate moieties is chelating whereas the other one is monodentate.

Cyclic *O,O*-alkylene dithiophosphato moieties may be sterically more demanding than their open chain analogues and variations in the structural features of their metal complexes may, therefore, also be expected. Our continuing interest in transition metal complexes of cyclic alkylene dithiophosphoric acids [11–15] led us to investigate the synthesis and structural elucidation of 2,9-dimethyl-1,10-phenanthroline adducts of bis(alkylene dithiophosphates) of nickel(II).

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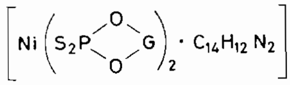
Results and Discussion

The 1:1 adducts of nickel(II) alkylene dithiophosphates with 2,9-dimethyl-1,10-phenanthroline



where G = $-C(CH_3)_2 \cdot C(CH_3)_2-$, $-(CH_3)_2C \cdot CH_2 \cdot CH(CH_3)-$ and $-CH(CH_3) \cdot CH(CH_3)-$ (Table 1), obtained by mixing the two components in dichloromethane in an equimolar ratio and cooling the solution, are dull/shining green crystalline compounds which are soluble in $CHCl_3$ and CH_2Cl_2 but insoluble in other solvents like carbon tetrachloride, benzene and alcohol. Like other heterocyclic ditertiary amine adducts [14], these are also stable in solution and do not show dissociation like monodentate nitrogen base adducts [12].

IR Spectra

IR spectra of these derivatives (Table 2) exhibit bands in the regions 1150–1055 and 870–860 cm^{-1} which may be assigned to (P)–O–C and P–O–(C) stretching modes respectively [16]. The bands present in the region 965–930 cm^{-1} may be ascribed to dioxaphospholane and dioxaphosphorinane ring vibrations [17, 18]. Interestingly, the P=S modes observed in the region 710–670 cm^{-1} in the spectra of *O,O*-alkylene dithiophosphoric acids and their ammonium salts are shifted to lower frequency (by ~30 cm^{-1}) in the spectra of the corresponding nickel(II) bis(alkylene dithiophosphates), are again shifted to higher frequency (by ~25 cm^{-1}) in the base adducts. The bands in the region 565–540 cm^{-1} are attributed to P–S symmetric and asymmetric vibrations (Table 2).

Magnetic Measurements

The values of magnetic moments at room temperature for 2,9-dimethyl-1,10-phenanthroline adducts of bis(tetramethylethylene dithiophosphato) nickel and bis(2,3-butylene dithiophosphato) nickel are 3.08 and 3.14 BM respectively which indicate the presence of two unpaired electrons [19].

Electronic Spectral Prpoerties

Electronic spectra in CH_2Cl_2 solution of these adducts, show two bands in the regions 668–670 nm and 432–440 nm. These electronic spectral transitions are characteristic of five coordinated Ni^{2+} ion [20].

Crystal Structure

The structure of the 2,9-dimethyl-1,10-phenanthroline adduct of bis(tetramethylethylene dithiophosphato) nickel(II) has been determined by single crystal X-ray technique. The coordination geometry is distorted trigonal bipyramidal. Out of four sulphur atoms of the two dithiophosphate moieties, three are bonded to the central nickel atom, showing unidentate behaviour of one of the dithiophosphate moieties and bidentate behaviour of the other. Two sulphur atoms S_1 and S_3 are in axial positions (S(1)-NiS(3) = 169.1°), the remaining one coordinated sulphur atom and two nitrogen atoms of 2,9-dimethyl-1,10-phenanthroline are occupying equatorial positions (S(4)NiN(1) = 144.3°, N(1)NiN(2) = 82.5° and S(4)NiN(2) = 131.1°). The coordination geometry of the analogous open chain, 2,9-dimethyl-1,10-phenanthroline adduct of bis(dimethyl dithiophosphato) nickel(II) has been reported by Shetty and Fernando [10] as intermediate between a tetragonal pyramid and trigonal bipyramid. However, they have not calculated the S(2)–Ni–S(3) angle. We have calculated this angle to be 166° from the data given in their paper [10]; this value comes quite close to 169.1° actually observed during the present studies in the anlogous cyclic compound. Various other bond angles and bond lengths reported in open chain analogoues are also quite akin to what we have observed in the case of the present cyclic derivative. The coordination geometry of both the derivatives could, therefore, be better understood in the form of a distorted trigonal bipyramidal geometry.

The atomic coordinates are given in Table 3 and the bond lengths and bond angles with their estimated standard deviations are given in Table 4. The structure has been shown in Fig. 1. Comparing the SPS angles in mono and bidentate dithiophosphate moieties the S(3)P(2)S(4) angle in the bidentate moiety is 108.0° and the S(1)P(1)S(2) angle in the monodentate moiety is 117.2°, indicating that the SPS angle is reduced on chelation. However, the OPO angle remains almost similar in both these cases.

Experimental

O,O-Alkylene dithiophosphoric acids, their ammonium salts and bis(alkylene dithiophosphato) nickel(II) were prepared by the methods reported earlier [11, 21].

Synthesis of Adducts

Reaction of bis(tetramethylethylene dithiophosphato) nickel(II) with 2,9-dimethyl-1,10-phenanthroline

A solution of 2,9-dimethyl-1,10-phenanthroline (0.343 g) in dichloromethane was added dropwise to a slurry of bis(tetramethylethylene dithiophosphato) nickel(II) (0.705 g) in the same solvent. The reaction mixture after heating for few minutes was kept at 0 °C. The green crystals of the 2,9-dimethyl-1,10-phenanthroline adduct of bis(tetramethylethyl-

TABLE 1. Adducts of nickel(II) *O,O*-alkylene dithiophosphates with 2,9-dimethyl-1,10-phenathroline

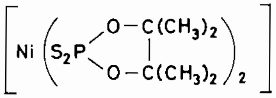
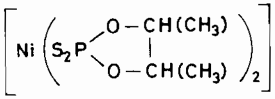
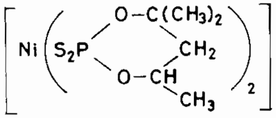
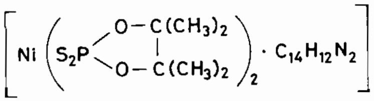
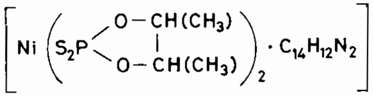
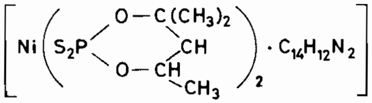
Bis(alkylene dithiophosphato)nickel(II)	2,9-Dimethyl-1,10-phenanthroline (g)	Yield of 1:1 adduct (g) (%)	Physical state Melting point (°C)	Analysis (%) found(calc.)	
				Ni	S
 (0.705)	0.343	0.980 95	Shining green crystalline compound (225)	8.38 (8.30)	18.5 (18.1)
 (0.649)	0.380	0.765 77	Light green powder (218)	9.14 (9.02)	19.5 (19.6)
 (0.544)	0.265	0.624 78	Green powder (220)	8.31 (8.30)	18.1 (18.1)

TABLE 2. IR spectral data of 2,9-dimethyl-1,10-phenanthroline adducts of nickel(II) bis(alkylene dithiophosphates)[a]

Compound	ν(P)–O–C	νP–O–(C)	Ring vibrations	νP=S	νP–S	νNi–S
	1150s	870m	930s	680s	565m	295w 380w
	1055m	870m	940s	715m	560w	
	1055m	860m	965s	680s	540w	310w 380w

[a] b, broad; m, medium; s, strong; w, weak.

TABLE 3. Fractional atomic coordinates (×10^4) with e.s.d.s in parentheses

	x	*y*	*z*
Ni	2759.6(6)	318.7(11)	10039.5(8)
S(1)	2677(1)	−1593(2)	9404(2)
S(2)	936(1)	−1422(3)	8423(2)
S(3)	3087(2)	2227(3)	10828(2)
S(4)	3975(1)	155(3)	10377(2)
N(1)	1969(4)	277(7)	10597(5)
N(2)	2040(4)	1107(7)	8974(5)
P(1)	1726(1)	−2266(2)	9219(2)
P(2)	4038(1)	1661(2)	11020(2)
O(1)	1776(3)	−3572(5)	8891(4)
O(2)	1613(4)	−2591(6)	10206(4)
O(3)	4506(4)	2590(7)	10718(6)
O(4)	4508(4)	1558(6)	12087(5)
C(1)	1952(5)	−191(9)	11410(7)
C(2)	1347(5)	−100(10)	11714(7)
C(3)	773(5)	500(9)	11183(7)
C(4)	783(5)	1000(9)	10328(7)
C(5)	203(5)	1629(9)	9712(8)
C(6)	234(5)	1997(10)	8863(8)
C(7)	838(5)	1816(9)	8577(7)
C(8)	894(6)	2160(9)	7687(8)
C(9)	1518(6)	1996(9)	7481(7)
C(10)	2099(6)	1459(9)	8164(7)
C(11)	1429(5)	1272(8)	9183(6)
C(12)	1402(5)	840(8)	10058(6)
C(13)	2604(6)	−788(11)	11981(7)
C(14)	2792(6)	1300(12)	8003(8)
C(15)	1714(6)	−3812(9)	10423(7)
C(16)	1544(8)	−4402(11)	9471(9)
C(17)	1864(7)	−5549(10)	9428(10)
C(18)	701(7)	−4521(14)	9028(11)
C(19)	1267(9)	−4134(14)	11043(10)
C(20)	2500(9)	−3937(15)	10999(13)
C(21)	5166(5)	2789(10)	11509(8)
C(22)	4978(7)	2533(12)	12392(10)
C(23)	5577(7)	2166(16)	13194(10)
C(24)	4592(7)	3539(14)	12676(11)
C(25)	5721(5)	1841(7)	11359(5)
C(26)	5368(9)	4051(14)	11380(14)

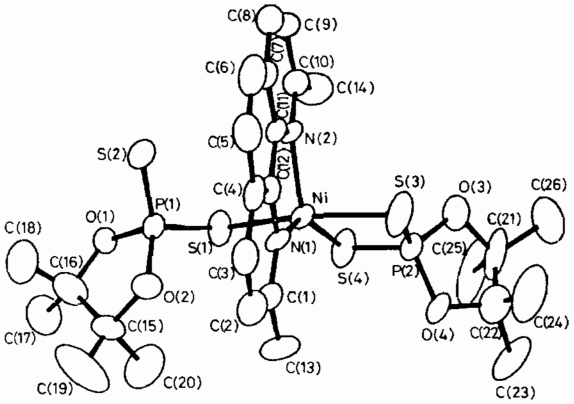


Fig. 1. Crystal structure of $C_{26}H_{36}NiN_2P_2O_4S_4$.

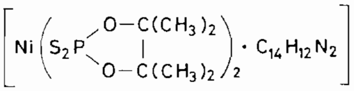
ene dithiophosphato) nickel separated out. These crystals after washing with acetone were dried under vacuum. See 'Supplementary Material'.

Relevant data for similar syntheses of other compounds are given in Table 1.

IR spectra were recorded as CsI pellets in the range from 4000–200 cm^{-1}. Electronic spectra were recorded in CH_2Cl_2 with an S.P. 8-100 UV–Vis Pye Spectrophotometer. Magnetic susceptibilities were determined by the Faraday method and diamagnetic corrections were calculated from Pascal's constant.

Crystal Structure Determination

A green crystal of



$$\left[\mathrm{Ni}\left(\mathrm{S_2P}\begin{matrix}\mathrm{O{-}C(CH_3)_2}\\ |\\ \mathrm{O{-}C(CH_3)_2}\end{matrix}\right)_2\cdot\mathrm{C_{14}H_{12}N_2}\right]$$

(0.25 × 0.15 × 0.15 mm) prepared as described above was sealed in a Lindemann glass capillary. Data were collected on an Enraf Nonius CAD4 diffractometer with monochromated Mo Kα radiation.

TABLE 4. Intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses

Bonds			
Ni–S(1)	2.398(3)	Ni–S(3)	2.499(3)
Ni–S(4)	2.344(3)	Ni–N(1)	2.005(8)
Ni–N(2)	2.015(7)	S(1)–P(1)	2.003(4)
S(2)–P(1)	1.936(3)	S(3)–P(2)	1.955(4)
S(4)–P(2)	1.979(4)	N(1)–C(1)	1.339(13)
N(1)–C(12)	1.347(11)	N(2)–C(10)	1.315(14)
N(2)–C(11)	1.368(13)	P(1)–O(1)	1.604(7)
P(1)–O(2)	1.602(7)	P(2)–O(3)	1.583(9)
P(2)–O(4)	1.591(7)	O(1)–C(16)	1.46(2)
O(2)–C(15)	1.453(13)	O(3)–C(21)	1.502(12)
O(4)–C(22)	1.46(2)	C(1)–C(2)	1.42(2)
C(1)–C(13)	1.498(14)	C(2)–C(3)	1.373(14)
C(3)–C(4)	1.41(2)	C(4)–C(5)	1.444(13)

(continued)

TABLE 4. *(continued)*

C(4)–C(12)	1.430(15)	C(5)–C(6)	1.36(2)
C(6)–C(7)	1.42(2)	C(7)–C(8)	1.42(2)
C(7)–C(11)	1.404(12)	C(8)–C(9)	1.39(2)
C(9)–C(10)	1.437(14)	C(10)–C(14)	1.49(2)
C(11)–C(12)	1.416(14)	C(15)–C(16)	1.52(2)
C(15)–C(19)	1.52(2)	C(15)–C(20)	1.56(2)
C(16)–C(17)	1.49(2)	C(16)–C(18)	1.63(2)
C(21)–C(22)	1.51(2)	C(21)–C(25)	1.627(15)
C(21)–C(26)	1.55(2)	C(22)–C(23)	1.48(2)
C(22)–C(24)	1.53(2)		
Angles			
S(1)–Ni–S(3)	169.1(1)	S(1)–Ni–S(4)	87.3(1)
S(1)–Ni–N(1)	100.0(2)	S(1)–Ni–N(2)	99.2(2)
S(3)–Ni–S(4)	82.1(1)	S(3)–Ni–N(1)	87.4(2)
S(3)–Ni–N(2)	89.6(2)	S(4)–Ni–N(1)	144.3(2)
S(4)–Ni–N(2)	131.1(3)	N(1)–Ni–N(2)	82.5(3)
Ni–S(1)–P(1)	111.3(2)	Ni–S(3)–P(2)	83.0(1)
Ni–S(4)–P(2)	86.7(1)	Ni–N(1)–C(1)	128.8(6)
Ni–N(1)–C(12)	111.9(6)	C(1)–N(1)–C(12)	119.3(9)
Ni–N(2)–C(10)	128.6(7)	Ni–N(2)–C(11)	111.2(6)
C(10)–N(2)–C(11)	120.3(8)	S(1)–P(1)–S(2)	117.2(2)
S(1)–P(1)–O(1)	105.4(3)	S(1)–P(1)–O(2)	111.1(3)
S(2)–P(1)–O(1)	113.9(2)	S(2)–P(1)–O(2)	111.4(3)
O(1)–P(1)–O(2)	95.6(4)	S(3)–P(2)–S(4)	108.0(2)
S(3)–P(2)–O(3)	111.6(3)	S(3)–P(2)–O(4)	115.4(4)
S(4)–P(2)–O(3)	114.7(4)	S(4)–P(2)–O(4)	110.5(3)
O(3)–P(2)–O(4)	96.5(4)	P(1)–O(1)–C(16)	112.4(7)
P(1)–O(2)–C(15)	112.6(7)	P(2)–O(3)–C(21)	109.8(7)
P(2)–O(4)–C(22)	112.7(7)	N(1)–C(1)–C(2)	121.1(8)
N(1)–C(1)–C(13)	116(1)	C(2)–C(1)–C(13)	122.4(9)
C(1)–C(2)–C(3)	120(1)	C(2)–C(3)–C(4)	119(1)
C(3)–C(4)–C(5)	124(1)	C(3)–C(4)–C(12)	117.0(8)
C(5)–C(4)–C(12)	119(1)	C(4)–C(5)–C(6)	120(1)
C(5)–C(6)–C(7)	121.4(9)	C(6)–C(7)–C(8)	123.8(9)
C(6)–C(7)–C(11)	120(1)	C(8)–C(7)–C(11)	116(1)
C(7)–C(8)–C(9)	119.9(9)	C(8)–C(9)–C(10)	120(1)
N(2)–C(10)–C(9)	120(1)	N(2)–C(10)–C(14)	117.3(9)
C(9)–C(10)–C(14)	122(1)	N(2)–C(11)–C(7)	123.8(9)
N(2)–C(11)–C(12)	116.7(7)	C(7)–C(11)–C(12)	119.5(9)
N(1)–C(12)–C(4)	122.9(9)	N(1)–C(12)–C(11)	117.5(9)
C(4)–C(12)–C(11)	119.6(8)	O(2)–C(15)–C(16)	104.7(8)
O(2)–C(15)–C(19)	108(1)	O(2)–C(15)–C(20)	105(1)
C(16)–C(15)–C(19)	117(1)	C(16)–C(15)–C(20)	112(1)
C(19)–C(15)–C(20)	109(1)	O(1)–C(16)–C(15)	103.6(9)
O(1)–C(16)–C(17)	110(1)	O(1)–C(16)–C(18)	107.1(9)
C(15)–C(16)–C(17)	118(1)	C(15)–C(16)–C(18)	109(1)
C(17)–C(16)–C(18)	108(1)	O(3)–C(21)–C(22)	105.2(9)
O(3)–C(21)–C(25)	105.4(8)	O(3)–C(21)–C(26)	104.5(9)
C(22)–C(21)–C(25)	110.5(9)	C(22)–C(21)–C(26)	116(1)
C(25)–C(21)–C(26)	114(1)	O(4)–C(22)–C(21)	101(1)
O(4)–C(22)–C(23)	109(1)	O(4)–C(22)–C(24)	110(1)
C(21)–C(22)–C(23)	114(1)	C(21)–C(22)–C(24)	112(1)
C(23)–C(22)–C(24)	110(1)		

Crystal Data

$C_{26}H_{36}NiN_2P_2O_4S_4$, M = 689.5, monoclinic, space group $P2_1/c$, a = 20.077(1), b = 11.599(2), c = 14.929(2) Å, β = 107.65(5)°, V = 3313.1 Å^3, Z = 4, D_c = 1.38 gm cm^{-3}, $F(000)$ = 1440, Mo Kα radiation, λ = 0.71069 Å, μ = 9.6 cm^{-1}. Data were collected in the $\theta-2\theta$ mode with $\Delta\theta = (0.8 + 0.35 \tan\theta)^0$ and a maximum scan time of 1 min. A total of 3383 unique reflections were measured for $2 < \theta < 20°$ and $+h +k \pm l$, and 2809 with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/L_p$. There was no crystal decay and no absorption correction was made.

The structure was solved by routine heavy atom methods and refined by full matrix least-squares with non-hydrogen atoms anisotropic. Hydrogen atoms were omitted. The weighting scheme was $w = 1/(\sigma^2(F))$ and the final residuals were $R = 0.070$, $R' = 0.090$. The final difference map was <0.9 e Å^{-3} throughout. Programs from the Enraf-Nonius SDP-Plus package were run on a PDP 11/34 computer.

Supplementary Material

Structure factors and thermal parameters are available from the authors on request.

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